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Wide Bandgap Semiconductor Nanowires for Electronic,Photonic and Sensing Devices

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**14. ABSTRACT**
We synthesized a variety of wide bandgap nanowires using GaN and ZnO and made functional devices from them for sensing,electronics and photonics.These included a very sensitive glucose sensor and hydrogen sensors with ppm sensitivity at room temperature.We also developed amorphous InZnO for transparent TFTs and showed highly stable operation.This effort grew out of the work on ZnO nanowires,where we noticed severe segregation effects when we tried to grow ternary wires.The IZnO films used for calibration showed very high mobilites and excellent

**15. SUBJECT TERMS**
GaN, ZnO, nanowires

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 15. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT | b. ABSTRACT | c. THIS PAGE | | | Stephen Pearton |
| UU | UU | UU | UU | | 19b. TELEPHONE NUMBER: 352-846-1086 |

**Report Title**

Wide Bandgap Semiconductor Nanowires for Electronic,Photonic and Sensing Devices


**ABSTRACT**

We synthesized a variety of wide bandgap nanowires using GaN and ZnO and made functional devices from them for sensing,electronics and photonics.These included a very sensitive glucose sensor and hydrogen sensors with ppm sensitivity at room temperature.We also developed amorphous InZnO for transparent TFTs and showed highly stable operation.This effort grew out of the work on ZnO nanowires,where we noticed severe segregation effects when we tried to grow ternary wires.The IZnO films used for calibration showed very high mobilites and excellent transparency.We were able to make TFTs on a wide range of substrates, including paper, plastic and clean room tape.


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## Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

**(a) Papers published in peer-reviewed journals (N/A for none)**

| Received | Paper |
|---|---|

**TOTAL:**

**Number of Papers published in peer-reviewed journals:**

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**(b) Papers published in non-peer-reviewed journals (N/A for none)**

| Received | Paper |
|---|---|

**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

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**(c) Presentations**

**Number of Presentations:** 0.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

| Received | Paper |
|---|---|

**TOTAL:**

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

| Received | Paper |
|---|---|

**TOTAL:**

**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):**

## (d) Manuscripts

| Received | Paper |
|---|---|

**TOTAL:**

**Number of Manuscripts:**

## Books

| Received | Paper |
|---|---|

**TOTAL:**

## Patents Submitted

## Patents Awarded

## Awards

2011 Bardeen award, TMS
2011 Adler award, APS
2011 Gordon Moore medal,ECS

## Graduate Students

| NAME | PERCENT_SUPPORTED | Discipline |
|---|---|---|
| Erica Douglas | 1.00 | |
| **FTE Equivalent:** | **1.00** | |
| **Total Number:** | **1** | |

## Names of Post Doctorates

| NAME | PERCENT_SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Names of Faculty Supported

| NAME | PERCENT_SUPPORTED | National Academy Member |
|---|---|---|
| S.Pearton | 0.08 | |
| **FTE Equivalent:** | **0.08** | |
| **Total Number:** | **1** | |

## Names of Under Graduate students supported

| NAME | PERCENT SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

| | |
|---|---|
| The number of undergraduates funded by this agreement who graduated during this period: ..... | 0.00 |
| The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... | 0.00 |
| Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): ..... | 0.00 |
| Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: ..... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ..... | 0.00 |

## Names of Personnel receiving masters degrees

| NAME |
|---|
| **Total Number:** |

## Names of personnel receiving PHDs

| NAME | |
|---|---|
| Erica Douglas | |
| Wantae Lim | |
| **Total Number:** | **2** |

## Names of other research staff

| NAME | PERCENT SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Sub Contractors (DD882)

**Inventions (DD882)**

**Scientific Progress**

We made significant progress in controlling the electrical and optical properties of a variety of wide bandgap nanowire systems and also found surprisingly high mobilities in amorphous IZO films ,which can be used as TFTs grown at room temperature on substrates such as glass and plastic.

(a) Nanowires

Background:

(i) GaN nanowires

Nanowires have attracted significant research attention in recent years due to their unique structural, electronic, optical, and mechanical properties. These properties make nanowires promising building blocks for potential applications such as transistors, lasers,photodetectors, and chemical and biological sensors.

There has also been significant recent interest in the development of hydrogen sensors for use in fuel cells as an energy source to replace petroleum. Since hydrogen is a hazardous, odorless, and highly flammable gas, hydrogen gas sensors play a critical role, particularly for fuel leak detection in spacecraft, automobiles, and aircraft, fire detectors, and diagnosis of exhaust and emissions from industrial processes. Nanowires are becoming promising candidates for H2 gas sensors due to their high surface to volume ratio. Wide bandgap semiconductors such as GaN and ZnO, have excellent potential for H2 gas sensing because of their sensitivity to surface charge and ability to operate over large temperature ranges. In addition, the use of a metallic coating can functionalize the surface of nanowires by dissociating H2 into
atomic hydrogen. While H2 sensors based on nanowires such as ZnO, SnO2, and In2O3 with excellent response and recovery characteristics have been reported in the literature, there have been few reports on H2 gas sensors based on GaN nanowires, which should offer excellent environmental stability.

Results:

We have grown the GaN nanowires by catalytic chemical vapor deposition (CVD) using gold thin films as catalyst on a Si wafer with an insulating SiO2 layer. The structural characterization of the as-grown nanowires by several methods shows that the nanowires are single-crystal wurtzite GaN. Photoluminescence measurements under 325 nm excitation show a
near-band-edge emission peak around
~3.4 eV. The hydrogen sensors are fabricated by contacting the as-grown GaN nanowires by source and drain electrodes and coating them with a thin layer of Pd. Hydrogen sensing experiments using the fabricated devices show high sensitivity response (ppm detection limit at room temperature) and excellent recovery. This work opens up the possibility of using high quality GaN nanowire networks for hydrogen sensing applications.

(ii) ZnO Nanowires:

Background:

ZnO is another wide bandgap materials that is attracting attention for application in transparent nanowire transistors because of the ease of synthesis of ZnO nanostructures, their good transport properties, the availability of heterostructures and the possibility for opto-electronic integration. A variety of both top and bottom gate n-type ZnO nanowire transistors have been reported, showing generally high on/off ratios (10^4-10^7), sub-threshold voltage swings of 130-300 mV/decade and excellent drain current saturation. Much higher electron mobilities and improved device stability are found when surface passivation is employed, pointing to the importance of controlling surface
charge density. Simulations show that defects such as grain boundaries lead to a decrease of drain current. While the dc characteristics of such devices are generally reasonable, there have been no reports of the rf or high speed switching performance. Additional work is needed on optimized gate dielectrics, reliability and functionality of ZnO nanowire transistors. There has been extensive interest in recent times in the synthesis of ZnO nanowires by a number of methods using both catalyst and catalyst-free approaches. Semiconductor nanowire device structures are expected to have potential advantages in improved carrier confinement over their thin film counterparts. The bandgap of the
ZnO may be increased by addition of Mg.

Results:

We recently developed a novel technique of selective-area growth of ZnO nanorods on the surfaces of other semiconductors or glass. Arrays of different patterns were easily fabricated with conventional photo-resist for masking. The resist patterned substrate was spin coated with ZnO nanocrystals used as seed materials. ZnO nanorods were grown in solution of 20 mM zinc nitrate hexahydrate
(Zn(NO3)2•6H2O) and 20 mM hexamethylenetetramine (C6H12N4) at 95 C. The concentration of reactants, pH and temperature were carefully controlled in a flask with polypropylene autoclavable cap for 3 hours growth. Subsequently, the substrate was removed from solution, thoroughly rinsed with de-ionized water to remove any residual salts and dried in air at the room-temperature. After nanorod growth, negative PR was removed with standard photoresist remover in a warm bath at 60 C for 30 minutes. Even though not shown here, the photoluminescence spectrum, obtained from the patterned ZnO nanorod area and substrate only at room temperature shows the free exciton emission at 3.24 eV. Also, the ZnO nanorods can be integrated with AlGaN/GaN HEMT sensors by incorporating the nano-rods on the HEMT gate sensing area, the total sensing area increases significantly. The conventional AlGaN/GaN HEMT detects the ambient changes through the “gate sensing area”. This area is defined as gate length × gate width in the regular HEMT. Although, we can increase the gate width to gain higher drain current from the transistor, the sensor detection sensitivity will be the same for HEMT with both short and longer gate width. This is due to the signal and background current proportionally increasing at the same time. Increasing the gate length will increase the parasitic resistance of the HEMT and the drain current decreases. Thus, the detection sensitivity goes down. Therefore, the only way to increase the sensitivity with the same ”gate dimension” is to grow 3D structures on the “gate sensing

area” to
increase the total sensing area with the area expansion to the third dimension. The ZnO nanorod matrix provides a microenvironment for immobilizing negatively charged GOx and retains its bioactivity, and passes charges produce during the GOx and glucose interaction to the AlGaN/GaN HEMT. With such low detection limit, it is possible to dilute <0.1 micro-liter of EBC in 100-200 micro-liter phosphate buffer solution (PBS) and directly measure the glucose concentration to eliminate the effect of pH variation. Due to the fast response time and low volume of the EBC required for the measurement, the technology can be realized as handheld and real-time glucose sensing .

(b) Flexible TFTs
Background:
Wide bandgap oxide-based thin film transistors (TFTs) have attracted much attention for applications like flexible electronic devices. The
fabrication of thin film transistors at low temperature on flexible substrates (e.g. plastic or paper) is a key technique to realize flexible electronics. So far, hydrogenated amorphous silicon (α-Si:H or organic semiconductor based TFTs have been widely used in display. However, they have some limitations, including light sensitivity and relatively low field effect mobilities (<1 cm2.V-1.s-1 for α-Si:H, ~ 2.7 cm2.V-1.s-1 for pentacene single crystals, and ~ 1.5 cm2.V-1.s-1 for pentacene thin films). A number of groups have demonstrated TFTs based on α-oxide semiconductors such as zinc oxide (ZnO), indium gallium oxide (InGaO), zinc tin oxide (ZnSnO), indium zinc oxide (InZnO)and indium gallium zinc oxide (InGaZnO). These materials showed surprisingly high electron mobilties (~ 10 cm2.V-1.s-1) even for α-films deposited near room temperature. High electron mobilities in the TFT channel translate to higher switching speeds of the devices. In addition, α-films have the potential for better TFT performance and stability than polycrystalline films because of the lack of grain boundaries in the channel. Amorphous-InGaZnO TFTs were first reported by Nomura et al. The concept of transparent amorphous oxide semiconductors (TAOS) with large electron mobilities was reported earlier. However, a typical problem with the oxide-based TFTs reported in the literature has been poor device stability. Recently, we have reported that α-InGaZnO-based TFTs fabricated on glass substrates show excellent long-term stability at room temperature.
Results:
High-performance amorphous (α-) InGaZnO-based thin film transistors (TFTs) were fabricated on flexible polyethylene terephthalate (PET) substrates coated with indium oxide (In2O3) films. We also achieved TFTs on clean-room tape and even paper substrates. The InGaZnO films were deposited by RF magnetron sputtering with the presence of O2 at room temperature. The n-type carrier concentration of InGaZnO film was ~2x1017 cm-3. The bottom-gate-type TFTs with SiO2 or SiNx gate dielectric operated in enhancement-mode with good electrical characteristics: saturation mobility 11.5 cm2.V-1.s-1 for SiO2 and 12.1 cm2.V-1.s-1 for SiNx gate dielectrics and drain current on-to-off ratio >105. TFTs with SiNx gate dielectric exhibited better performance than those with SiO2. This is attributed to the relatively high dielectric constant (i.e. high-k material) of SiNx. After
more than 500 hours aging time at room temperature, the saturation mobility of the TFTs with SiO2 gate dielectric was comparable to the as-fabricated value and the threshold voltage shift was 150 mV.

## Technology Transfer